RELATIVE REACTIVITIES IN THE DIRECT OXIDATION OF BINARY HYDROCARBON FUELS ON PRACTICAL ELECTRODES

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INTRODUCTION

The direct oxidation of hydrocarbon fuels in presence of aqueous electrolytes and at temperatures less than 200°C has been extensively studied.[1] The interest of investigators has been mainly focused on pure paraffinic hydrocarbons. However, practical hydrocarbon fuels will probably be rather complex or at least consist of binary or ternary mixtures. If the reactivity of these fuels differs appreciably it can be expected that preferential anodic oxidation will correspond to the depletion of the more reactive species at the detriment of others. This, in turn, will result in an enrichment of the less reactive species. In addition, competitive adsorption and reactions are expected to take place on the electrode surface. These processes are not well known for complex mixtures. Relative reaction rates will also depend on anodic potentials, resulting in varying fuel reactivity, as the electrode surface potential varies with over-all currents.

The design of multi-cell stacks operating with fuel mixtures could be based on the least reactive species; gains in cell performance could be obtained if the behavior of various fuels could be understood.

It was decided to approach the problem by studying binary systems such as propane/octane, hexane/octane and heptane/octane. Individual constituents of these binary mixtures have been extensively investigated, and anode performance as a function of molecular chain length has shown that at 150°C in presence of phosphoric acid the fuel reactivity varies as: propane>hexane>heptane>octane.[2]

EXPERIMENTAL

The experimental work was conducted on porous platinum electrodes (geometric area: 50 cm^2) prepared according to techniques described elsewhere.[3] Phosphoric acid was used as the electrolyte at 150°C and concentrations ranging from 95-97 wt.%. High acid concentrations were chosen in order to operate the fuel at relatively low water vapor pressures, in equilibrium with the electrolyte. The electrolyte was pumped in the cell at flow rates sufficiently large to avoid thermal and concentration gradients. The counter-electrode operated on oxygen or air. Isothermal conditions were obtained by placing the complete cell in an oven, maintaining the cell temperature at 150 ± 2°C. Figure 1 represents

the single cell. Single electrode potentials (with and without
ohmic contributions) were measured by means of a hydrogen re-
ference electrode, located in the same environment (same tem-
perature and electrolyte concentration).

The fuel (pure grade 99.9 mole %) was pre-mixed be-
fore entering the anode compartment. The fuel system, single-
pass type, allowed the exit stream to enter a Perkin-Elmer 801
gas chromatograph, provided with a "hot" gas sampling valve and
thermal conductivity cell. The chromatograph was calibrated
with about 50 samples of chemical species and mixtures of species
to determine separation time, peak heights, areas and the proper
temperature of the column. The calibration was based on the area
under the "peak" as described by a mechanical integrator on a Leeds-
Northrup recorder.

Specific calibrations were conducted with known quantities
of carbon monoxide, carbon dioxide, propane, hexane, octane, methane,
air and mixtures of these constituents for a six foot, 1/8 inch O.D.
column, packed with silica gel. Separation of air, carbon monoxide
and methane could be accomplished at room temperature; carbon
dioxide and propane at 150°C, and hexane and octane at 250°C. The
carrier gas was helium, set at 30 cc/min. at 150°C, and although
the chromatograph had flow compensators to keep carrier flow con-
stant through the programmed temperature excursion the flow de-
creased somewhat at 250°C. Error was minimized by calibrating the
chromatograph and running a fuel cell sample under the same condi-
tions of temperature programming.

It was necessary to heat the sample valve, the sampling
tube, and all fuel exhaust lines that were exposed to room ambient
in order to prevent condensation of the higher boiling constituents.
The lines were kept constant at about 150°C and monitored by thero-
couples in various locations.

The anode exhaust was directed to a heated Teflon de-
humidifier containing two chambers, one which trapped electrolyte
leakage, and the other which contained phosphorous pentoxide to
remove water vapor from the fuel exhaust before introduction to
the silica gel column. The small fuel flows (approximately 0.02
cc/min.) were fed through a capillary tube flowmeter and the rates
determined from pressure drops.

A schematic illustration of fuel feed and exhaust for
the chromatograph system is shown in Figure 2. Helium was used
to pressurize the fuel tank because its presence in the fuel would
not be detected by the chromatograph. Pressure fluctuations due
to the helium regulator were dampened by bleeding part of the helium
to a water column. The bypass allowed the fuel feed line to the
cell to be quickly filled prior to testing. The liquid fuel mixture
was vaporized inside the oven in coaxial metal tubes, the inner
tube supplying fuel to the hot outer tube, where it was "flash" vapor-
ized. The system provided very satisfactory operation, with re-
producible calibration and smooth, steady flow.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Fuel and Oxidant Migration

Although fuel and oxidant solubilities are rather low at 150°C in concentrated phosphoric acid[4] (0.18 millimoles of propane/liter-atm., 0.34 millimoles of oxygen/liter-atm., approx. 0.03 millimoles of octane/liter-atm.), measurements were conducted to determine the rate of fuel loss and carbon dioxide evolution at the anode, due to chemical oxidation of the fuel. Results are reported in Table I.

Table I

Transport of Chemical Species Across the Electrolyte[*]

Species at source electrode	Species at Counter-electrode	Transport Rate (moles/cm^2-sec-atm) x 10^{10}
Octane	Helium	1
Octane	Oxygen	1
Carbon dioxide	Helium	4
Oxygen	Propane + Octane	52

[*]Electrode size: 50 cm^2. Electrolyte spacing: 3.2 mm. Phosphoric acid conc. 95-97 wt.% at 150°C. Species at source electrode at 1.0 atm.

In the case of oxygen transport measurements, the dissolved air in the fuel (about 0.2 mole %) was not a contributing factor to the oxygen content of the anode stream.

2. Electrochemical Oxidation of Pure Octane

Octane, at open circuit, showed a carbon dioxide content in the anode exhaust of 1%. If this is assumed to be chemical combustion from oxygen migrating from cathode to anode, it corresponds to a parasitic current density of 0.3 ma/cm.^{2} Pure octane, at 20 ma/cm^2 showed a fuel utilization and carbon dioxide production within 2% of the theoretical value. Corrected for chemical combustion, the agreement was within 1%.

3. Binary Fuel Mixtures

Attempts made to detect hydrogen, carbon monoxide or species other than the fuels fed into the anode chamber, were negative. Interfering peaks observed at low retention times, were identified as oxygen and/or nitrogen, due to oxidant migration from cathode to anode.

a. Propane/octane fuel mixtures.

The experimental results are reported in Figure 3

for the current contribution of propane as a
function of log mean mole fraction of propane
in the anode chamber. (Inlet concentrations
are determined by flow rates, exit concentrations
by gas chromatographic analysis. All data are
corrected for the vapor pressure of water in
equilibrium with the electrolyte.) The rate of
propane oxidation is proportional to the mole
fraction in the feed stream and also strongly
dependent on the anodic potential, e.g. increasing
the anodic potential induced a decrease in anodic
propane current. This observation is in con-
tradiction with the behavior of pure propane for
increasing anodic potentials, at least up to potentials
corresponding to oxygen deposition on the electrode
surface. Linearity between propane current and
gas phase composition is obtained up to average mole
fractions of 0.3 to 0.4. At higher concentration,
the electrode current is due entirely to the oxida-
tion of propane. Similar observations can be made
for octane, although the current due to octane
oxidation increases with increasing anodic overvoltage,
as expected. The behavior of this binary mixture
is suggestive of species interaction and competition
on the electrode surface.

Propane and octane currents can be represented by:

$$i_3/I = 740 \ e^{-11.6\eta_{X_3}} \qquad\qquad 1.$$

and

$$i_8/I = 0.06 \ e^{6.0\eta_{X_8}} \qquad\qquad 2.$$

where x_3 and x_8 represent the log mean mole fraction of propane
and octane in the gas phase. At anodic over-potentials of 0.5
volts vs. H^+/H_2, at which most of the experimental data was ob-
tained, the currents can be expressed as:

$$i_3/I = 2.2 \ x_3 \qquad\qquad 3.$$

and

$$i_8/I = 1.2 \ x_8 \qquad\qquad 4.$$

b. Hexane/octane fuel mixtures.

All results reported in Figure 4 were obtained at
anodic potentials near 0.5 volts vs. H^+/H_2, necessary
to achieve current densities up to 40 ma/cm^2. Approxi-
mate linear relationships between current and gas phase

composition are obtained. The relative current contribution of octane is identical to that obtained for the binary propane-octane mixture. (i_8/I) is expressed by equation 4; for hexane:

$$i_6/I = 4.0 \ x_6 \qquad\qquad 5.$$

c. Heptane/octane fuel mixtures.

The trends are similar to those obtained for the other binary mixtures (Figure 5). The current contribution of octane can be expressed by equation 4; for heptane:

$$i_7/I = 2.5 \ x_7 \qquad\qquad 6.$$

4. <u>General Relations</u>

At high anodic overvoltage (0.5 volts vs. H^+/H_2) all current contributions can be represented by:

$$i_n/I = K \ x_n \qquad\qquad 7.$$

where K represents a "fuel reactivity constant" representative of the molecular chain length of the paraffinic hydrocarbon.

Table II

Fuel Reactivity Constants for Various Fuels (at 0.5 volts vs H^+/H_2)

Fuel	K-Value
Propane	2.2
Hexane	4.0
Heptane	2.5
Octane	1.2

These results are presented in Figure 6. For hexane, heptane and octane the current contribution can be predicted from:

$$i_n/I = (13-1.5 \ n) \ x_n \qquad\qquad 8.$$

where n represents the number of carbon atoms in the molecular chain. From pure fuel reactivity data reported by others[2], the expected reactivity constant for propane should be approximately $k_3 = 5.7$, whereas the measured value in the propane/octane mixture is only 2.2. This result may indicate competitive surface processes between hydrocarbon species of rather dissimilar chain lengths. C_1 and C_2 paraffinic hydrocarbons are expected to be less reactive than propane. C_9 and C_{10} n-paraffins are not expected to yield reactivity

constants appreciably different from n-octane.

The experimental results are presented in Figure 7 in terms of corrected current contributions, i.e. $i_n/13-1.5$ n) I vs. gas phase composition (using the experimental value of $K_3 = 2.2$ for propane). At present, the exact physical significance of the fuel reactivity coefficient is not clear.

CONCLUSION

The anodic electrochemical oxidation of binary fuel mixtures of hexane, heptane and octane can be predicted from the fuel gas phase composition and the relative reactivity of these fuels, which decreases with increasing chain length. The behavior of propane in propane/octane mixtures is unexpected, the propane reactivity decreasing with increasing anodic overvoltage.

ACKNOWLEDGMENT

REFERENCES

1. Hydrocarbon-Air Fuel Cells, U.S. Army Engineer Research and Development Laboratories, Ft. Belvoir, Va., Contract No. DA-44-009-ENG-4909 and DA-44-009-AMC-479(T) - Reports 3 to 6.

2. Ibidem, Report No. 4

3. Niedrach, L.W. and H.R. Alford, Abstract No. 23, ECS Meeting, 1964, Washington, D.C.

4. Same reference as 1 - Report No. 6

PICTORIAL VIEW OF HYDROCARBON AIR LIQUID ELECTROLYTE FUEL CELL TEST FIXTURE, SHOWING FLUID STREAMS

1 ELECTROLYTE SPACER
2 GASKET
3 ELECTRODE
4 GASKET
5 GAS SPACER
6 DIFFUSER CLAMP
7 GASKET
8 DIFFUSER
9 GASKET
10 DIFFUSER CLAMP
11 GASKET
12 GAS END PLATE ADAPTER
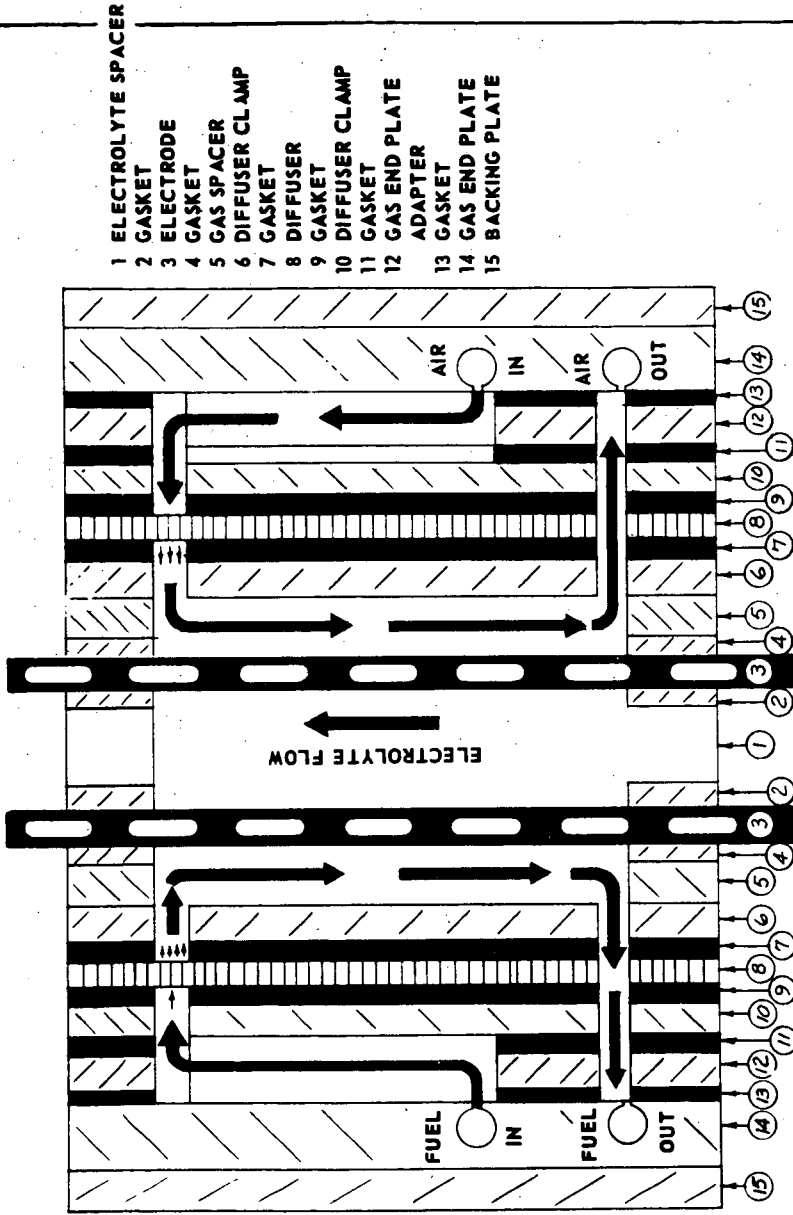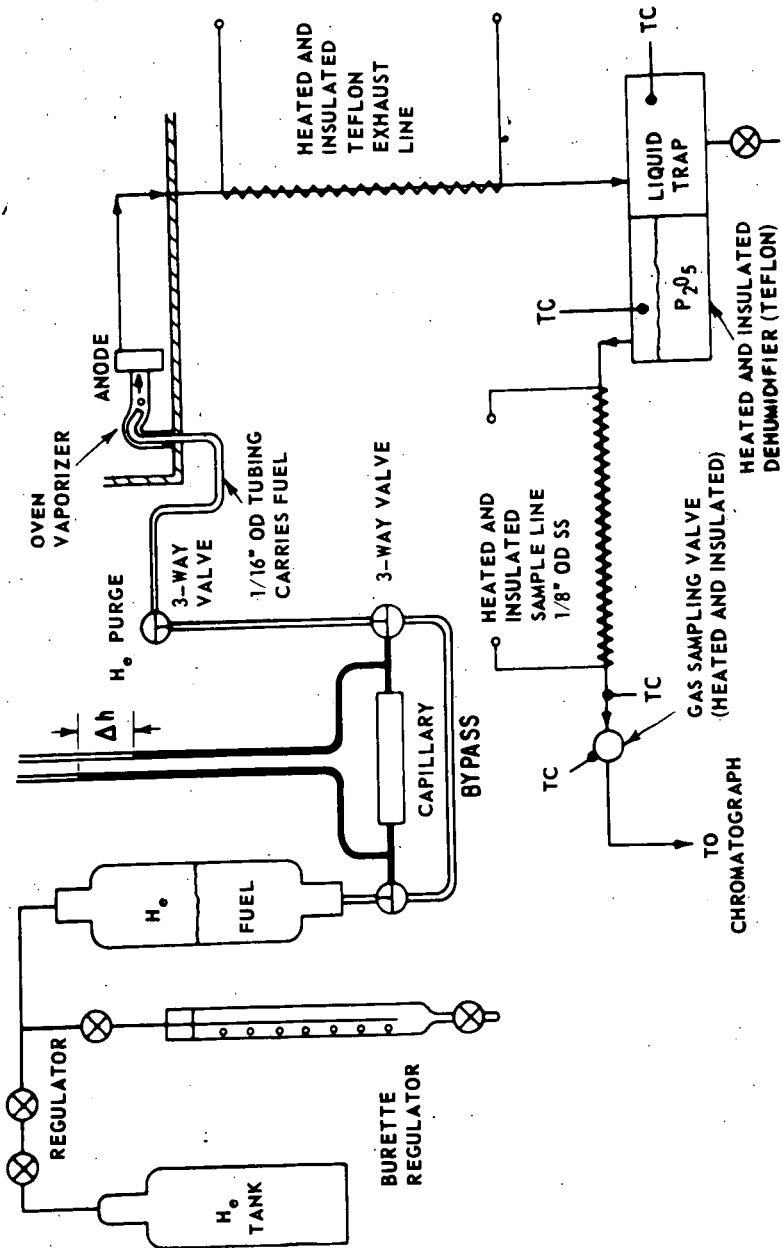13 GASKET
14 GAS END PLATE
15 BACKING PLATE

FIGURE 1

FIGURE 2   FUEL FEED AND EXHAUST FOR CHROMATOGRAPH
SYSTEM FOR THE STUDY OF BINARY FUELS.
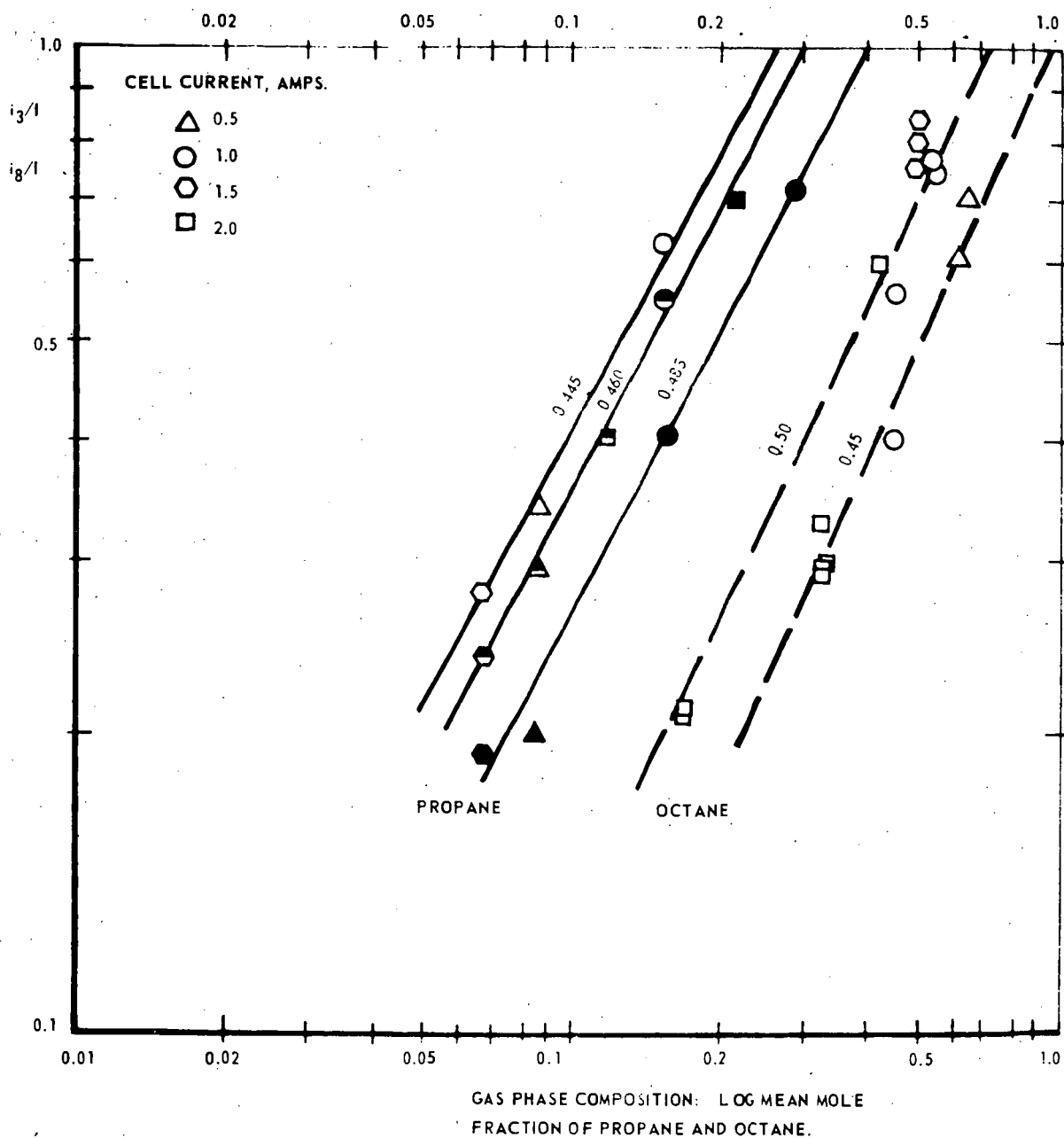
FIGURE 3: RELATIVE CURRENT CONTRIBUTION OF PROPANE AND OCTANE AS A FUNCTION OF ANODE POTENTIAL.
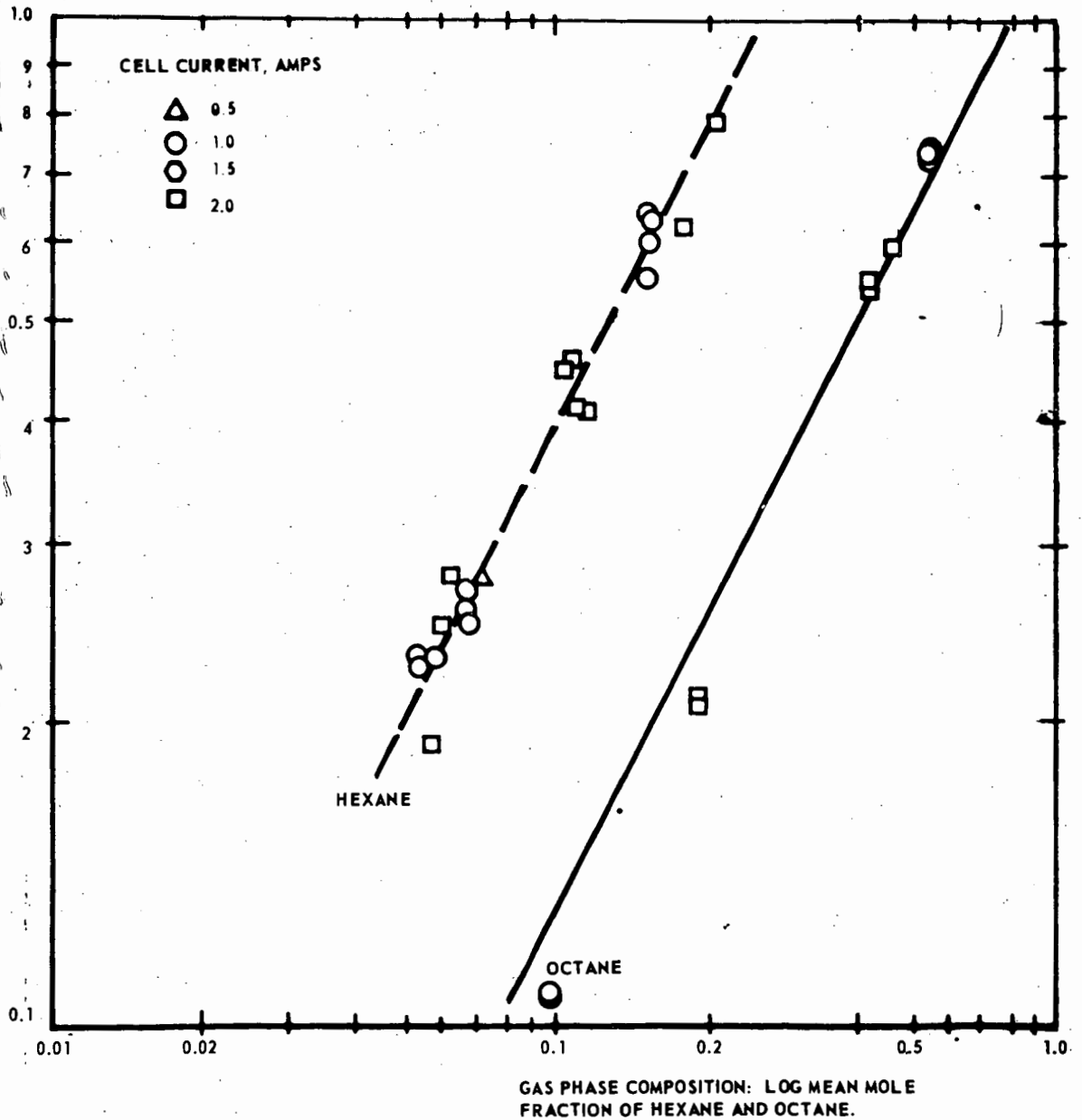
FIGURE 4: RELATIVE CURRENT CONTRIBUTION OF HEXANE AND
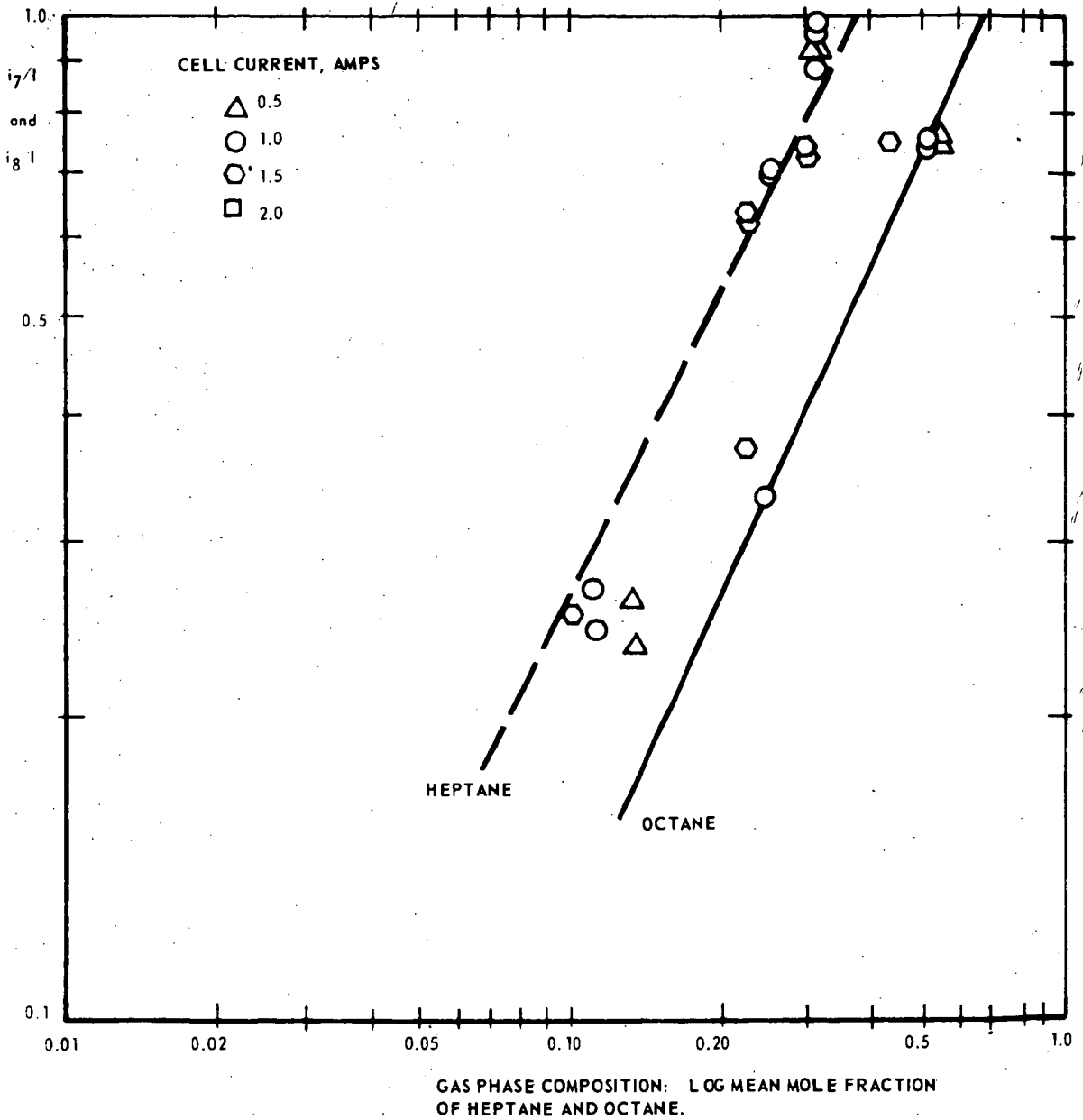OCTANE AT APPROX. 0.5 VOLTS ANODIC POTENTIAL.

GAS PHASE COMPOSITION: LOG MEAN MOLE FRACTION
OF HEPTANE AND OCTANE.

FIGURE 5: RELATIVE CURRENT CONTRIBUTION OF HEPTANE AND
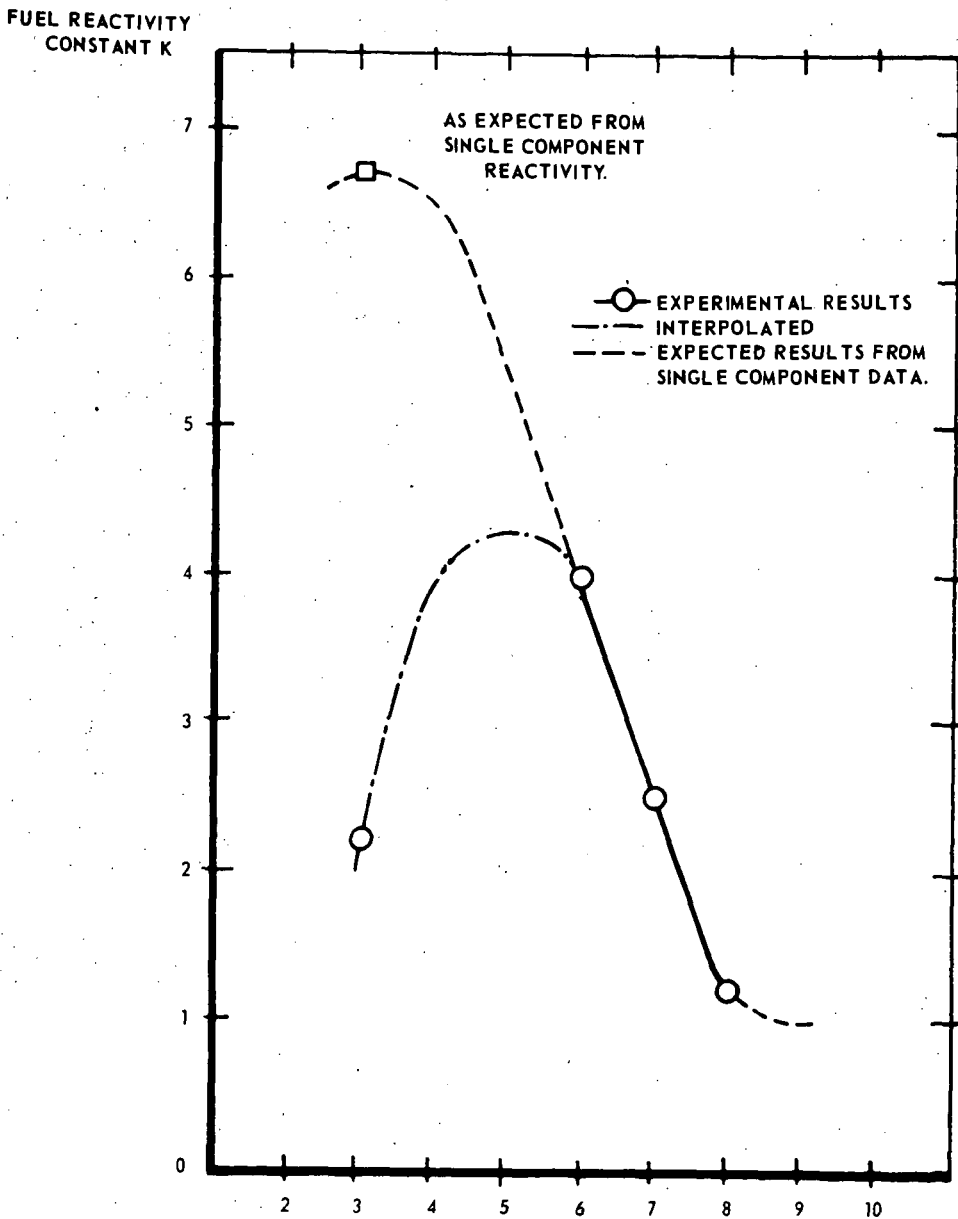OCTANE AT APPROX. 0.5 VOLTS ANODIC POTENTIAL.

FIGURE 6: DEPENDENCE OF THE FUEL REACTIVITY CONSTANT K
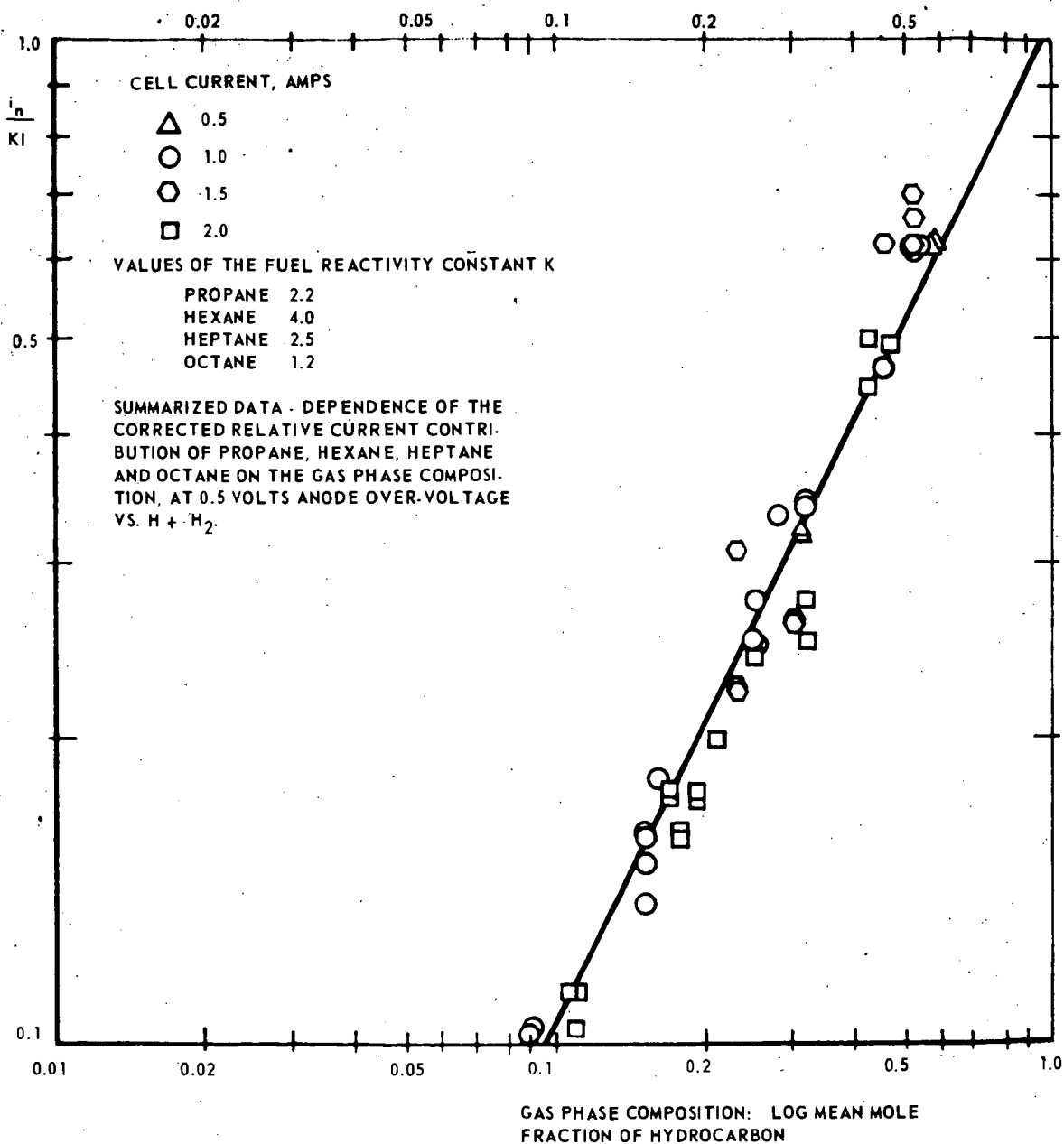ON THE HYDROCARBON CHAIN LENGTH.

GAS PHASE COMPOSITION: LOG MEAN MOLE
FRACTION OF HYDROCARBON

FIGURE 7